The Osmotic Pressure of Dilute Benzene Solutions by the Porous Disk Method

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

L. C.

BY

WILLIAM CUSTER EICHELBERGER

Baltimore, 1930

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ACKNOWLEDGMENT

The writer wishes first of all to express his sincere gratitude to his parents who made it possible for him to pursue his studies toward a higher degree.

He wishes further to express his great appreciation to Dr. J. C. W. Frazer and Dr. W. A. Patrick who suggested the problem and under whose kindly direction, counsel and encouragement it was carried out.

He wishes to thank Dr. D. H. Andrews for his advice in designing the new method of temperature control apparatus; and Mr. W. A. Patrick, Sr., for his assistance in the mechanical construction of much of the equipment for the thermostats and other apparatus. Many thanks are also due Dr. F. T. Martin and Dr. L. H. Schultz for their kindly advice and aid in the designing and construction of the apparatus. Finally, the writer wishes to thank other members of the faculties of Chemistry and Physics who have offered assistance at one time or another during the pursuit of the problem.

The drawings of the apparatus were made by Mr. K. W. Flocks.

THE OSMOTIC PRESSURE OF DILUTE BENZENE SOLUTIONS BY THE POROUS DISK METHOD

Introduction

An accurate method of measuring a colligative property (1) of very dilute solutions in order to test the Debye–Hückel theory of solutions at low concentrations and (2) of colloidal solutions is very desirable. Heretofore, none of the colligative properties could be investigated at sufficient dilutions for these purposes. Furthermore, a method is needed which is applicable over a range of temperature, concentration and kind of solvents. Osmotic pressure is one property which can be so studied.

Measurements of osmotic pressures of non-aqueous solutions have been very few, due mainly to the fact that no suitable membrane could be found. Usually the membrane either dissolved slightly in the solvent, or was nearly impermeable to it. A brief survey of the work with non-aqueous solvents is given by Bartell and Osterhof[1] and also by Murray.[2]

In order to overcome the difficulties of membranes in osmotic pressure measurements Townend,[3] working under the direction of Professors J. C. W. Frazer and W. A. Patrick, developed a new method of measuring these pressures in which the ideal membrane is used, that is, the vapor of the solvent itself. It is known as the "porous disk method" of measuring osmotic pressures and should be applicable to solutions of any volatile solvent and non-volatile solute. The method was improved by Martin and Schultz.[4] The apparatus used in the present series of measurements was designed after that used by the latter two workers, with the neces-

[1] F. E. Bartell and H. J. Osterhof, *Coll. Sym. Mon.*, **4**, 234 (1926).
[2] M. J. Murray, *J. Phys. Chem.*, **33**, 896 (1929).
[3] R. V. Townend, *J. Am. Chem. Soc.*, **50**, 2958 (1928).
[4] F. T. Martin and L. H. Schultz, *J. Phys. Chem.*, **35**, 638 (1931).

sary modifications and improvements needed for use with non-aqueous solvents.

Temperature Regulation

In this method of measuring osmotic pressures it is very essential that the temperature of the osmometer (the instrument used to measure the osmotic pressure), including all parts having the vapor state in contact at any point with either the solution or the solvent, be kept very constant throughout the measurement of a tension (see Frazer and Patrick[5] and Martin[6]).

For this purpose there was constructed a large thermostat 127 cm. high by 86 cm. in diameter, heavily insulated with hair-felt. Instead of the usual type of toluene–mercury thermoregulator, which has presented a number of difficulties when attempts have been made to secure regulation better than 0.001°, a new method of temperature control, proposed by Dr. D. H. Andrews of this Laboratory, was tried. Using the principle of the Wheatstone bridge, a resistance thermometer was constructed of four 900-ohm coils, alternately nickel and constantan. No. 36 nickel wire was used and No. 30 constantan. Each coil was wound on a sheet of asbestos board 15 × 15 × 0.32 cm. The four coils were mounted in a thin, water-tight copper shield filled with transformer oil. This was suspended in the thermostat in a location similar to that of the osmometer flask. The wires from the coils were led through a brass tube to the top of the thermostat. An e. m. f. of 12 volts was impressed across two sides of the bridge and a sensitive galvanometer was connected across the other two sides. A change in temperature unbalanced the bridge, causing the mirror of the galvanometer to move. Light was reflected from this mirror upon a photoelectric cell in such a manner as to move on the cell when the thermostat cooled down and to move off when it warmed up. The weak current of the cell was amplified by a vacuum tube and relays which cut on and off the current to the electric heater in the thermostat.[7]

A stream of water, several degrees cooler than the main thermostat and held constant to ±0.02° by means of a small auxiliary thermostat, was circulated continuously through a coil in the center of the bottom of the main thermostat.

With this method of temperature control, regulation to ±0.002° was the best which could be secured. Applying the principle of the Gouy oscillating contact[8] for toluene–mercury thermoregulators, a "shutter," consisting of a metal strip 5.2 × 7.6 cm., was suspended in front of the photoelectric cell in the path of the beam of light. This shutter was connected to a crank on a reducing gear-box driven by an electric motor. Its amplitude was less than the operating width of the photoelectric cell and its frequency was about 45 cycles per minute. It operated in such a manner that, as the thermostat cooled down, the beam of light shone on the cell for larger fractions of each cycle; and as the thermostat warmed up, the light hit the cell for smaller fractions of each cycle. When the temperature of the thermostat became very constant, the beam of light was practically stationary, shining on the position of the cell all the time and being cut off from the cell by the shutter at definite intervals. By this method it was possible to hold the temperature constant to ±0.0002°, or better, for several hours at a time.

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[5] J. C. W. Frazer and W. A. Patrick, *Z. physik. Chem.*, **130**, 691 (1927).

[6] F. T. Martin, "Dissertation," Johns Hopkins University, 1929.

[7] Details of this method of temperature regulation have appeared in the literature since this work was done.

[8] Sligh, *J. Am. Chem. Soc.* **42**, 60 (1920); also Gouy, *J. phys.*, **6**, 479 (1897).

A differential thermometer, consisting of a capillary of a 360° thermometer sealed to a number of short, parallel tubes filled with an alcoholic solution of a dye, was used to read the temperature variations in the thermostat to 0.0002°.

Glass Apparatus.—The main change in the glass apparatus over that used by Martin and Schultz[4] with aqueous solutions was the elimination of all stopcocks where they might in any way come in contact with benzene, the solvent in the present experiments, because stopcock grease is soluble in benzene. This required an additional valve in the mercury traps. The osmometer was also changed slightly.

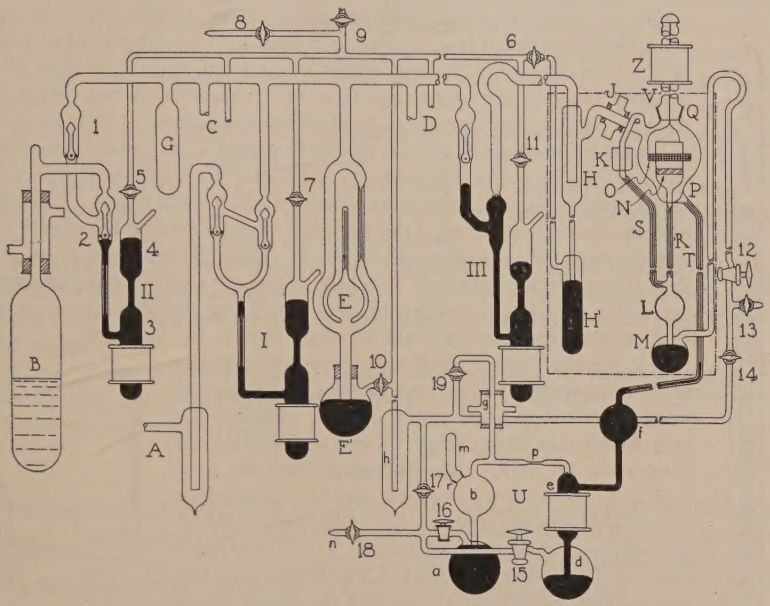

Fig. 1.

A diagram of the apparatus is shown in Fig. 1. The trap A, cooled with solid carbon dioxide, led to a two-stage mercury diffusion pump backed by a Cenco Hyvac oil pump. The mercury trap I connected the pumps to the main system. A bulb B of about 800-cc. capacity was a benzene reservoir. Another such bulb and trap were connected at D. At C was connected a mercury trap like trap I and a new type of deaerating apparatus. E was a McLeod gage. G was a 60-cc. bulb for condensing benzene vapor in the main system and as an approximate measure of benzene for diluting the solutions. Mercury trap III led to the apparatus in the thermostat. H was a mercury cut-off in the thermostat for enclosing the vapor system entirely under water.

The main part of the apparatus, that used for the measurements, was the "osmometer." It consisted of a liter flask, P, inside of which was sealed a cup containing the porous disk, N. Near the top of the flask was a tube connecting it to the trap H. Over this tube was a small condenser, J, for distilling benzene into the solution. On the upper side of the tube, near the osmometer, was connected a small tube leading to the capillary S and around which was another condenser, K, which was used to distil benzene under the disk. Into the top of the osmometer was fitted a ground-glass, mercury-sealed stopper, Q, sealed to a tube, V, shown in detail in Fig. 2. In V was mounted the

mechanism for operating the stirrer, O, in the solution. O was a platinum gauze bent in a circle around the cup containing the disk. Platinum wires supporting the gauze were welded together above the cup and hooked over F, a tungsten wire sealed into a glass rod, Y.

Martin and Schultz[4] observed during their measurements that liquid condensed in the tube containing the stirrer mechanism, at the point where the tube came through the water of the thermostat, and which caused an erroneous rate of distillation. Hence, a mercury seal had to be placed inside this tube. The detail of V, Fig. 2, shows the inverted glass cup at W fitted over a small tube. The cup was sealed to a glass rod, Y, which was sealed to a glass tube containing a bar of iron, X. The entire stirrer was suspended from a phosphor-bronze spring supported at the top of V. The bottom of the cup rested in mercury, thereby sealing off the benzene vapor in the osmometer from the remainder of the stirrer tube. This cup was below the water level of the thermostat. The stirrer was operated by means of a solenoid mounted around V just below the center of the iron bar, X. The solenoid was connected to the 14-volt line and in series with an eccentric driven by a motor and reducing gears. This cut on and off the current through the solenoid, thereby pulling the stirrer down and up and hence agitating the solution. The inverted cup was raised and held above the mercury seal by means of the solenoid when the osmometer was being evacuated or when benzene was being distilled into it in order that pressure equilibrium could be established in the top of V.

Fig. 2.—Stirrer mechanism.

R was the "inner" and S was the "outer" capillary of the osmometer. These two capillaries formed the manometer for measuring the osmotic pressure and they were about 65 cm. long. R was sealed to the cup supporting the disk. R and S met above the small bulb L whose mercury reservoir was M. A capillary tube T led from the solution side of the osmometer to the solution-introducing apparatus, U. These capillaries and the osmometer flask as high as the disk were visible from outside the thermostat through a narrow window. Doors in front of the window insulated it from without.

All the apparatus within the broken line in Fig. 1 was inside the thermostat and below the water level.

The Porous Disk.—A description of the porous disk, used to support the pure solvent and made from equal parts of Pyrex glass and a special clay, is given by Martin and Schultz.[4]

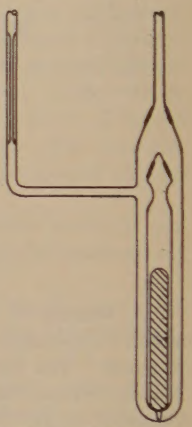

Fig. 3.—Valve for mercury traps.

Mercury Traps.—The mercury traps were similar to those designed by Martin and Schultz[4] except for the extra valve necessary for the elimination of a stopcock in contact with mercury. This valve (bulb 3, Fig. 1, and shown in detail in Fig. 3) was a ground-glass stopper sealed to a glass tube containing a bar of iron. This stopper, which floated in mercury, fitted into its ground-glass seat at the top of the bulb. It was pulled down by passing a current through a solenoid mounted around the bulb, 3.

To close the trap, atmospheric pressure was admitted to bulb 4, Fig. 1, through stopcocks 5 and 8 and the stopper in 3 was pulled down by passing a current through the solenoid. Then the mercury was allowed to rise in 2 until the stopper was seated and mercury-sealed. To open the trap, the procedure was the same except that instead of

atmospheric pressure, vacuum from an oil pump for the "secondary system" was admitted to bulb 4 through stopcocks 5 and 9.

The mercury for the traps was purified by allowing it to drop through a long column of dilute nitric acid and then through distilled water, and finally distilling it under vacuum. The mercury for the bulbs of the osmometer and of the solution-introducing apparatus was similarly purified, except that it was redistilled three times.

The Solute

The solute used in osmotic pressure measurements by this method obviously must be as non-volatile as possible. Inorganic salts are the most desirable to use because of their low vapor pressure, but unfortunately very few of them are soluble to any extent in benzene. Furthermore, many of those which are soluble are associated in benzene solution.

An organic compound of high molecular weight and of high boiling point was selected as the solute: tetraphenylethylene. It melts at 221°, boils at 425° ("International Critical Tables") and has a molecular weight of 332.16. Hence it was felt that its vapor pressure at 25° and in dilute solutions would be sufficiently low for use in the present experiments. It is very soluble in benzene.

A freezing-point lowering determination of it in 0.1 molar benzene solution was made and it was found to behave normally. Its calculated molecular weight was 320.4 which, for the method employed, was considered within experimental error of the theoretical value.

The tetraphenylethylene had been carefully purified by Smith[9] for specific heat measurements. It gave a good freezing-point curve, so no further purification of the substance was deemed necessary.

Experimental

Purification and Deaeration of the Benzene.—The benzene used was Baker's C. P. benzene. It was purified according to Dr. Greer's method[10] and was stored over calcium chloride. Just before use the benzene was distilled off phosphorus pentoxide, the fraction boiling within 0.04° or less, of the boiling point being collected.

About 400 cc. of this benzene was poured into the bulb B, Fig. 1, and subsequently frozen. The top of the bulb was then sealed off and most of the air pumped out of the bulb. The benzene was further cooled with solid carbon dioxide and the space above it in the bulb was highly evacuated. After closing trap II, the benzene was allowed to melt. Water was circulated through the condenser above the bulb and a small electric light beneath the bulb supplied heat for refluxing the benzene. At frequent intervals the air above the benzene in the bulb was expanded into the outer evacuated system by closing trap I and opening trap II. The benzene could not be opened directly to the pumps, as there would have been a very rapid distillation of benzene into the solid carbon dioxide trap, A. This process was repeated for a number of days until less than 0.001 mm. of mercury air pressure developed overnight. This benzene was then distilled into another bulb connected to the main system and containing phosphorus pentoxide by placing ice around the phosphorus pentoxide bulb and warm water around the bulb B and opening the proper traps. The benzene was refluxed over the phosphorus pentoxide for about a week to dry it completely and remove the last traces of sulfur impurities. Then the benzene was distilled back into the first bulb and its deaeration was continued for several weeks until the air pressure which accumulated above it after stand-

[9] Smith, "Dissertation," Johns Hopkins University, 1930.

[10] E. Juanita Greer, *J. Am. Chem. Soc.*, **52**, 4191 (1930).

ing two days was of the order of 10^{-5} mm. of mercury. Thereafter, the air was removed at less frequent intervals.

A new deaerator, designed by Dr. Taylor[11] of this Laboratory for the preparation of air-free liquids, was used in the deaeration of the benzene for the last experiment.

Cleansing and Deaeration of the Osmometer.—The osmometer, before mounting in the thermostat, was treated with a saturated solution of chromic oxide in concentrated nitric acid for four days, allowing the solution to run through the disk to the bulbs below. Then it was cleaned with dilute nitric acid for a day. It was then washed with distilled water and finally with conductivity water until the water which ran through the disk had practically the same conductivity as that put in the flask above the disk.

The osmometer was evacuated continuously for a couple of days to remove most of the air. Then benzene from one of the reservoir bulbs was distilled into it by closing trap I, opening the main system to one of the benzene reservoirs and running ice water down the sides of the osmometer flask in order to remove the last traces of grease and impurities in the flask. After admitting air to the osmometer, this wash benzene was drained out. The disk and disk cup also were carefully rinsed with pure benzene.

The osmometer was reëvacuated for several days, at the end of which time an air pressure of only 2×10^{-4} mm. of mercury developed upon standing overnight. Air-free benzene from one of the reservoir bulbs was then distilled into the bulb below the disk by running ice water through condenser K, and then the benzene was raised upon the mercury from the bulb M into the space under the disk. By pumping this benzene through the disk, out of the osmometer, most of the air left in the disk was removed and afterwards an almost negligible air pressure developed in the osmometer, which was now ready for measurements.

Procedure in Making Measurements.—Air-free benzene from a reservoir bulb was distilled under the disk by a method similar to that by which Martin and Schultz introduced water under the disk in their apparatus.[4] When sufficient benzene had been placed under the disk the mercury in R (and S) was pumped up by pumping air through stopcocks 13 and 12 until most of the benzene had been forced through the disk.

Air which had accumulated in the osmometer during this distillation was removed by evacuating the main system to a flat gage and then expanding the air in the osmometer into the evacuated system. After letting the benzene stand over the disk for half a day, the liquid was pulled down slowly through the disk by placing small tensions (two centimeters of mercury) upon the benzene; that is, by lowering the mercury level in the outer capillary S a couple of centimeters below that in R. After all the benzene had been pulled through the disk, it was possible to place tensions up to 60 cm. of mercury upon the pure benzene without its breaking away from the disk.

Next, the solution was introduced into the osmometer, using the apparatus shown at U, Fig. 1. A solution of the desired concentration and volume was prepared under as dry conditions as possible. The benzene was protected from moisture by transferring it from one flask to another through small tubing and drying with phosphorus pentoxide the air which was used to force over the liquid.

The solution-introducing apparatus was evacuated to dry the bulbs completely and the mercury. Air was readmitted to it through trap *h* which was surrounded with solid carbon dioxide. The solution was transferred from the flask in which it had been prepared into the bulb *b*, taking precautions to exclude as much moisture as possible. After mercury-sealing the stopper *m* at *r*, ice water was circulated through the condenser *g* and the solution was partially evacuated by opening and closing stopcock 19 frequently. This stopcock could not be left open continuously, or too much benzene would have distilled into the solid carbon dioxide trap, *h*.

[11] R. K. Taylor, *J. Am. Chem. Soc.*, **52**, 3576 (1930).

When most of the air had been removed from the solution, the mercury in T and *f* was lowered until the stopper in the valve *e* was released from its seat. The solution in *b* was then raised slowly by admitting air to the mercury bulb *a*, thereby forcing the solution into *f*, stopping before the mercury ran from *b* to *e*. Then air was admitted to *d* slowly, which forced the stopper in *e* into its seat and raised most of the solution into the osmometer. By means of a hand air pump, air pressure was pumped into *d* sufficient to force all the solution and about 100 cc. of mercury into the osmometer flask. The solution was floated on mercury to give better thermal equilibrium between the solvent under the disk and the thermostat. The mercury level was just below the disk. In this manner was introduced into the osmometer 200 cc. of solution.

The deaeration of the solution was completed in the osmometer by repeatedly expanding the air into the outer evacuated system until no air pressure in the system was observed when it was tested with the McLeod gage. The stirrer for the solution was started and the air was again removed until an air pressure of the order of only 10^{-5} mm. of mercury developed after several hours of stirring.

Meanwhile, the thermoregulator equipment was set in operation. When the temperature had been regulating for an hour to within $\pm 0.0005°$ or less, measurements of the osmotic pressure of the solution were begun. Temperature variations of less than $\pm 0.0002°$ were secured part of the time and gave much more reliable results.

Various tensions were placed upon the pure solvent and their corresponding rates of distillation were measured. Using tensions less than that corresponding to the osmotic pressure of the solution, distillation from the solvent to the solution took place; conversely, using tensions greater than that corresponding to the osmotic pressure of the solution, distillation from the solution to the solvent occurred. Distillations in both directions were measured in order to keep the concentration of the solution as nearly the same as possible; however, the maximum amount of benzene distilled in either direction was never over several tenths of a cubic centimeter.

Positions of the upper meniscus (that in the capillary R under the disk) and of the lower meniscus (that in the outer capillary S) were read to hundredths of millimeters with a cathetometer, and the times of reading the upper meniscus were noted. A reference line on the apparatus was also read each time because the apparatus shifted slightly and all the readings had to be corrected to the initial, or "zero," position of the osmometer.

After applying a tension, about an hour was allowed before readings were begun, in order that constant conditions would be established. Three readings of each meniscus and reference line were made at approximately hourly intervals. After determining the average of each set of readings, the height through which the upper meniscus had moved was calculated. This height was immediately plotted against its corresponding time. When three or four points lying approximately on a straight line were obtained, the slope of the best line drawn through them gave the rate of distillation for that tension and further readings on that tension were discontinued. A new tension was then applied and its rate was determined. The rates were plotted against their corresponding tensions and a line was drawn through these points. When a straight line was obtained from a number of rates, the measurements on that solution were complete. The point at which the line crossed the zero-rate axis gave the tension corresponding to the osmotic pressure of the solution—the observed osmotic pressure.

The tension exerted upon the pure solvent is made up of three parts: (a) the length of the mercury column from the lower to the upper meniscus; (b) the benzene column from the upper meniscus to the surface of the disk; and (c) the net height of benzene vapor from the surface of the disk

to the surface of the solution, which, from equilibrium considerations and the laws of thermodynamics, must be equal to a benzene column of the same height. The mercury equivalents of parts (b) and (c) were calculated and added to (a) to determine the actual tension on the solvent.

The mean time for the tension and the mean position of the lower meniscus were determined for the points used in drawing the rate curve. All calculations were made at the temperature of the thermostat, namely, 26.85°.

The theoretical value of the osmotic pressure was calculated from the equation

$$PV_0 = xRT = (N/N_0)RT, \text{ or}$$
$$P = NRT/V_0N_0$$

where P = osmotic pressure in atmospheres, V_0 = molar volume of solvent, x = mole fraction of solute, N = number of moles of solute, N_0 = number of moles of solvent, R = gas constant and T = absolute temperature.

After starting a series of measurements, readings were taken on as many tensions as possible, usually three or four, so long as the thermostat was working properly. From four to six hours were needed for the measurement of each tension.

Analysis of Solution.—After completing the measurements of the tensions, three samples of the solution were removed for analysis in order to determine its concentration. The same apparatus that was used for introducing the solution was used for removing it. The solution was lowered into bulb *f*, Fig. 1, and then permitted to run slowly from *f* to *b*, by lowering the mercury level in *e* sufficiently to release the stopper in *e* from its seat. When enough solution had run into *b*, the remainder was forced back into the osmometer. After admitting air to *b* and removing the stopper *m*, the solution was sucked from *b* into three glass-stoppered flasks which held about 50 cc. each.

The weight molar concentration of the solution was determined by weighing (1) the flask and solution, (2) the flask and solute after evaporating off the solvent, and (3) the empty flask after dissolving out the solute and drying the flask.

Dilution of the Solution.—Knowing the approximate concentration of the solution in the osmometer, from the way in which it had been prepared, it was possible to calculate the approximate amount of solution which must be removed from the osmometer to leave the correct amount of solute for the next lower concentration. This calculated amount was the volume removed for analysis and was divided into the three samples. Also, this was the volume of pure benzene which had to be added to the solution for the next dilution.

To dilute the solution the outer system was evacuated to a flat gage,

trap I was closed and trap II was opened. Ice water was placed around bulb G and the benzene for diluting the solution was distilled from a reservoir bulb into G. Trap II was closed when the proper amount of benzene was in G. Traps III and H were opened, water at a temperature of 31–35° was placed around G and ice water was circulated through condenser J. This caused the benzene to distil from G to J and from there it ran into the solution. Reflux action between the benzene under the disk and the condenser J caused benzene to be distilled from under the disk into the solution. This was later replaced by more benzene.

When the dilution was completed, traps III and H were closed. The outer system was evacuated to a flat gage and any air in the osmometer was removed by repeated expansions into the outer evacuated system. The stirrer in the solution was set in motion and when the solution was as air-free as possible, measurements on this concentration were made.

Experimental Results

A preliminary experiment was performed using pure benzene as the "solution" in order to test the possibilities of the apparatus and to learn how to manipulate it. Then the osmotic pressures of five solutions of tetraphenylethylene in benzene were measured, starting with the most concentrated solution and diluting down. The results of these experiments are given in Table I. The concentrations are weight molar and the osmotic pressures are millimeters of mercury at the temperature of the experiments, 26.85°.

The results of one experiment are given in detail in Table II. In the columns are listed, from left to right, the times at which the upper meniscus was read, the positions of the upper meniscus, of the lower meniscus and of the reference line, and the temperature variations of the thermostat as observed during the course of the experiment. Data for the other experiments were recorded in the same way.

TABLE I

Experiment number	Concentration, weight molar	Osmotic pressure, mm. Observed	Calculated
2	0.01919	313.2	312.7
3	.01502	242.9	244.8
4	.01007	162.1	164.1
5	.004057	66.7	66.1
6	.000466	10.5	7.6

As explained previously, from these data were calculated the distances through which the upper meniscus moved. By plotting these results the osmotic pressures, that is, the tensions for zero rates of distillation, were determined.

Figure 4 is a graph of the height–time curves for Table II, illustrating the method of determining the rates of distillation. Figure 5 is a graph

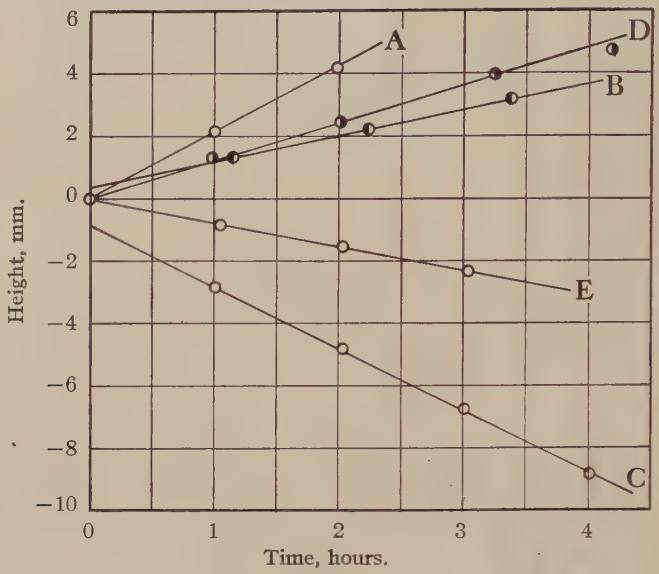

Fig. 4.

of the rate–tension curves for all the experiments, from which the osmotic pressures for Table I could be read. From this last figure one may observe the nearness of the points obtained to their respective lines and

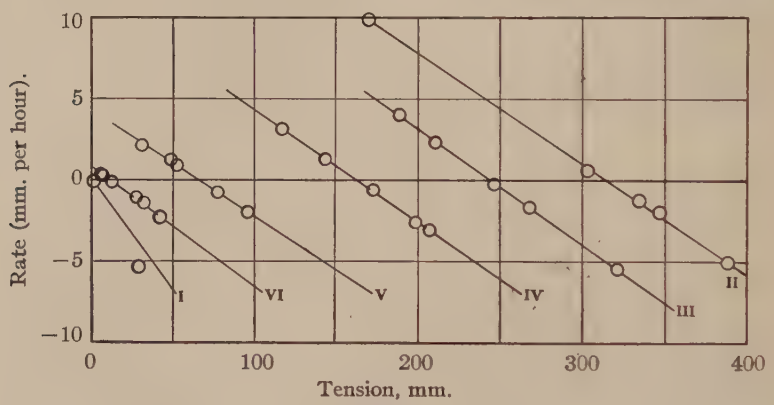

Fig. 5.

hence the relative accuracy of the results. The results of experiments 2 to 5 are within 1% of their values as calculated from the equation $PV_0 = xRT$. The result of the last experiment has about the same absolute

error as some of the others, but its percentage error is much greater because of the very dilute solution.

TABLE II

Concentration (weight molar)..... 0.004057
Temperature (average)..... 26.851°
Osmotic pressure (mm. of mercury, 26.85°), Observed..... 66.7 mm.
Calculated..... 66.11 mm.

Tension A

Time, hours	Upper meniscus, mm.	Lower meniscus, mm.	Reference line, mm.	Temperature variations, °C.
0	409.68	417.15	215.99	±0.0005
1.007	407.40	417.29	216.00	± .0002
1.985	405.21	417.27	216.01	± .0001

Average tension (mm. of mercury).....35.41 mm.
Rate of distillation.....+2.12 mm./hr.

Tension B

0	353.95	382.73	215.97	±0.0002
1.151	352.68	382.75	216.11	± .0005
2.236	351.63	382.86	216.00	± .0002
3.386	350.56	382.90	215.95	± .001

Average tension (mm. of mercury).....53.23 mm.
Rate of distillation.....+0.82 mm./hr.

Tension C

0	353.91	432.60	215.99	±0.0002
1.002	356.93	432.96	215.98	± .0002
2.034	359.02	433.23	215.97	± .0004
3.007	361.08	433.41	215.96	± .0002
4.005	363.40	433.59	215.99	± .0003

Average tension (mm. of mercury).....95.71 mm.
Rate of distillation.....−1.99 mm./hr.

Tension D

0	361.52	384.95	215.93	±0.0004
0.984	360.21	385.33	216.00	± .0002
2.010	358.91	385.57	215.94	± .0005
3.244	357.43	385.74	216.11	± .001
4.182	356.45	385.96	215.93	± .0005

Average tension (mm. of mercury).....48.48 mm.
Rate of distillation.....+1.21 mm./hr.

Tension E

0	360.00	416.16	215.87	±0.0006
1.044	360.92	416.13	215.89	± .0002
2.032	361.72	416.18	215.97	± .0004
3.038	362.56	416.19	215.96	± .0002

Average tension (mm. of mercury).....77.48 mm.
Rate of distillation.....−0.76 mm./hr.

By examining the graphs and the data sheets it was observed that in nearly every case where a point did not fall on or very close to the line drawn through the other points there were temperature variations greater than $\pm 0.0005°$ in the thermostat. Very small temperature fluctuations would tend to compensate each other to some extent, but this was not usually the case with larger ones.

Considering the behavior of the apparatus and the results obtained, the author considers the apparatus suitable for measuring the osmotic pressures of dilute solutions over a certain range of concentration, the upper value of which is governed by the length of the capillary tubes R and S in the osmometer, Fig. 1. Better temperature regulation must be secured before very dilute solutions, those below 0.001 molar, can be measured accurately.

Summary

1. An apparatus was developed with which it was shown possible to measure, with a fair degree of accuracy, the osmotic pressures of dilute solutions, benzene solutions of tetraphenylethylene being those measured. Greater precision should be possible if better temperature regulation could be secured.

2. A new type of thermoregulator employing a resistance thermometer and photoelectric cell was constructed for accurately controlling the temperatures of thermostats.

3. The elimination of stopcocks in vacuum systems containing vapors which will dissolve stopcock grease was successfully accomplished by means of a modification of mercury traps.

BIOGRAPHY

William Custer Eichelberger was born November 18, 1906, in Pana, Illinois. He began his public school education in Pana, attended a public school in Los Angeles for one term, and completed his elementary education in Dresden, Ohio. He graduated from Jefferson High School, Dresden, Ohio, in 1923 and entered Oberlin College in the fall of that year. He received a B.A. degree from Oberlin College in 1927 and has pursued graduate work in chemistry at The Johns Hopkins University since then. He held University Scholarships in 1928–29 and 1929–30.